



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(54) Title: LOW DENSITY POLYETHYLENE POLYMER BLEND AND STRETCH WRAP FILM APPLICATION (57) Abstract  A polymer blend comprising a linear low density polyethylene, further including from 0.5 to 5 % (w/w) of a low density polyethylene wherein said low density polyethylene has a long-chain branch frequency of greater than 2 /1000C and a molecular weight fraction (M<sub>w</sub>) over 5 x 10<sup>5</sup> g/mol of greater than 2.5 % by weight of the low density polyethylene, and further including an effective amount of a cling additive. The polymer composition may be used in films particularly suited for stretch wrap applications, and also particularly in monolayer films for stretch wrap applications.</p>		

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## LOW DENSITY POLYETHYLENE POLYMER BLEND AND STRETCH WRAP FILM APPLICATION

The present invention relates to a polymer composition for use in films particularly suited for stretch wrap applications, and also to a modified linear low density polyethylene for use in  
5 monolayer films for stretch wrap applications.

Pallets containing smaller packages are regularly stabilised using polymer films. While shrink wrapping has been used, the more economic and safer process of stretch wrapping is presently being adopted for the stabilisation of pallet loads of packages and other packaging  
10 applications. Stretch wrap films incorporate a cling additive that binds each layer of film so that effectively a single unit is obtained and the inherent elasticity of the film provides a rebound force which prevents a load shifting during storage and transport.

Stretch wrap films desirably have a number of attributes including high resistance to puncture  
15 and tear when stretched and under tension, high elastic rebound, high adhesion between layers of stretched film, high degree of prestretching possible prior to wrapping of the articles, and good optical properties. In order to obtain improvements in some or all of these film properties, multilayer film structures have been employed.

20 Linear low density polyethylene (LLDPE) has been adopted for stretch wrap applications due to its combination of a number of the desirable properties described above. Linear low density polyethylenes used for blown film stretch wrap applications are typically produced by solution polymerisation using octene as the comonomer. Linear low density polyethylene may also be produced by gas phase polymerisation, for example, using hexene as a  
25 comonomer. LLDPEs produced by gas phase polymerisation have a molecular structure which mitigates against the use of these LLDPEs in blown film stretch wrap applications. Gas phase polymerisation processes using hexene as a comonomer provide a linear low density polyethylene which is particularly suited for cast stretch wrap applications. However its use in blown stretch wrap applications is limited.

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We have now found that by modifying linear low density polyethylene it is possible to obtain a blown stretch wrap film monolayer having improved properties which render it particularly suited for stretch wrap applications. In the context of LLDPEs produced by gas phase polymerisation the modification according to the present invention allows the gas phase  
5 polymerized LLDPEs to be used advantageously in stretch wrap applications. In the context of LLDPEs generally, the modification according to the present invention provides the LLDPEs with improved properties, such as improved migration of cling additive to the surface of the film and an increase in the amount of pre-stretching possible.

- 10 According to the present invention there is provided a polymer blend comprising a linear low density polyethylene, further including from 0.5 to 5% (w/w) of a low density polyethylene wherein said low density polyethylene has a long-chain branch frequency of greater than 2 /1000C and a molecular weight fraction ( $M_w$ ) over  $5 \times 10^5$  g/mol of greater than 2.5% by weight of the low density polyethylene, and further including an effective amount of a cling  
15 additive.

According to a further aspect there is provided a monolayer film manufactured from a polymer blend comprising a linear low density polyethylene, further including from 0.5 to 5% (w/w) of a low density polyethylene wherein said low density polyethylene has a long-  
20 chain branch frequency of greater than 2 /1000C and a molecular weight fraction( $M_w$ ) over  $5 \times 10^5$  g/mol of greater than 2.5% by weight of the low density polyethylene, and further including an effective amount of a cling additive.

It will be understood that the term, "linear low density polyethylene" is meant to include  
25 copolymers of ethylene and at least one alpha-olefin comonomer. The term includes copolymers, terpolymers, etc. Linear low density polyethylenes are generally copolymers of ethylene and alpha-olefins such as propene, butene, 4-methyl-pentene, hexene, octene and decene.

30 Linear low density polyethylenes suitable for use in the present invention include those

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produced by commercial polymerisation processes such as gas phase polymerisation, slurry polymerisation and solution polymerisation, including multireactor systems of any combination of these processes. Catalysts suitable for use in the production of linear low density polyethylenes include homogeneous and heterogeneous catalysts.

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Linear low density polyethylenes generally have a density in the range of from 910 to 960 kg/m<sup>3</sup>. Typically, linear low density polyethylenes suitable for blown film extrusion have a melt flow index (MFI) in the range of from 0.1 to 7.0 g/600s.

10 Linear low density polyethylenes typically have peak melting points in the range of from 110 °C to 130 °C. The heat of fusion of linear low density polyethylenes is typically in the range of from 18 to 42 cal/g. Linear low density polyethylenes typically have a crystallinity in the range of from 25 to 60%.

15 Preferred linear low density polyethylenes for use in the present invention are polymerized in gas-phase reactors using heterogeneous catalysts. The preferred linear low density polyethylene is polymerized in a gas-phase reactor using a Ziegler/Natta catalyst system. Such preferred polymers preferably have a density in the range of from 913 to 930 kg/m<sup>3</sup> and a melt index in the range of from 0.4 to 2.5 g/600s. Solution-phase and slurry-phase  
20 polymerized linear low density polyethylenes may also be used advantageously in the polymer blends of the present invention.

Low density polyethylenes suitable for use in the present invention include ethylene homopolymers and copolymers having up to 30% (w/w) of a comonomer such as vinyl  
25 acetate, butyl acrylate and the like. Low density polyethylenes most suitable for use in the present invention are produced by free radical polymerisation via a high pressure autoclave process. Preferably the low density polyethylenes for use in the present invention are polymerised under conditions which are known to those skilled in the art to favour the production of polymers with broad molecular weight distributions and a high degree of long-  
30 chain branching such as in an autoclave reactor. It is particularly preferred that the low

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density polyethylenes have a bi-modal molecular weight distribution and a high degree of long-chain branching in the high molecular weight fraction of the low-density polyethylene.

The low density polyethylenes generally have peak melting temperatures in the range of from 80 °C to 115 °C. Typically their heat of fusion is in the range of from 18 to 30 cal/g and their crystallinity is in the range of from 20 to 45%.

Preferably the low density polyethylenes selected for use in the compositions of the present invention have melt indices in the range of from 0.1 to 7 g/600s, more preferably 0.3 to 4 g/600s. Preferably the low density polyethylenes have a density in the range of from 913 to 930 kg/m<sup>3</sup>, more preferably in the range of from 917 to 922 kg/m<sup>3</sup>. Preferably the low density polyethylenes have a polydispersity index ( $M_w/M_n$ ) of greater than 15 and more preferably greater than 22. The  $M_z$  value of low density polyethylenes is preferably greater than  $2 \times 10^6$  g/mol, more preferably greater than  $3 \times 10^6$  g/mol. The long-chain branch frequency as determined by <sup>13</sup>C nuclear magnetic resonance spectroscopy is greater than 2 /1000C and preferably greater than 3 /1000C. The high molecular weight fraction over  $M_w$   $5 \times 10^5$  is greater than 2.5%, preferably greater than 5%, and more preferably greater than 10% of the total LDPE polymer by weight.

The cling additive for use in the present invention may be any suitable cling additive. Examples of suitable cling additives include migratory tackifying agents such as low molecular weight polyisobutylenes or polybutenes, atactic polypropylenes, glycerol monooleate and sorbitol monooleate. Preferably, the cling additive is a low molecular weight polyisobutylene, such as a poly(isobutylene-co-butylene) having a number average molecular weight in the range of from 300 to 5000 g/mol. More preferably the low molecular weight polyisobutylene has a molecular weight in the range of from 500 to 3000 g/mol.

The cling additive is present in the modified linear low density polyethylene in an effective amount, preferably in the range of from 0.1 % to 7 % (w/w).

The polymer blends according to the present invention may include a variety of other additives such as those known to persons skilled in the art. Such additives include process, thermal, light and weathering stabilisers, pigments and dyes, surface friction modifiers and the like.

5

The polymer blends of the present invention may be compounded on a variety of extrusion equipment such as is well known to those skilled in the art. Extrusion equipment is generally capable of providing dispersive and distributive mixing capabilities. Suitable extrusion equipment includes single and multi-screw extruders, multi-rotor type extruders and the like.

10 Preferably the polymer blend is blended on a twin-screw extruder. While such continuous processing equipment is generally preferred it is possible to form the polymer blends of the present invention in batch processes.

The polymer blends of the present invention may be mixed and blended in an extruder which  
15 is ultimately used in the film blowing process if it is equipped with screw mixing elements, static mixer units, gear pumps or combinations of such mixing units capable of providing sufficient dispersive and distributive mixing. Preferably the polymers and additives used to form the polymer blend of the present invention are blended in a separate process using a single or multi-screw extruder specifically designed for compounding polymer blends. Most  
20 preferably, the polymers and additives used to form the polymer blends of the present invention are compounded ex-LLDPE reactor on a co-rotating twin-screw extruder in an inert atmosphere and the subsequently formed polymer blend is pelletised for use in a separate film manufacturing process.

25 The manufacture of film suitable for use in stretch wrap applications may be performed in blown film and cast film processes which are well known to those skilled in the art. Blown film processes are preferred in the manufacture of stretch wrap applications using polymer blends of the present invention. The addition of cling additives such as polyisobutylene is usually conducted by injection into the extruder between the feed throat and the compression  
30 zone of the screw using a metering pump. Careful control over the addition rate of the

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polyisobutylene, the film cooling rate and the film winding tension are required to provide optimum properties in the stretch wrap film. Such film manufacturing techniques are well known to those skilled in the art.

- 5 The polymer blend of the present invention permits the manufacture of stretch wrap film having substantially improved properties. The cling additive in the stretch wrap film manufactured from a polymer blend according to the present invention advantageously exhibits faster and more consistent migration to the surface of the film, particularly in gas-phase polymerised linear low density polyethylene, immediately after manufacturing thereby
- 10 allowing a reduction in the storage time required before such films are suitable for use. Prior art films generally require storage in excess of 7 days prior to use.

Films manufactured from the polymer blend of the present invention may advantageously demonstrate improved retention of cling properties subsequent to the film being stretched.

- 15 The improved retention of cling is particularly evident once the film has been stretched to over 250% of its original length with the consequent reduction in thickness. The integrity of films manufactured from polymer blends of the present invention is substantially improved and can be seen in the ability of the films to maintain the loading even at higher stretch ratios. The ability to stretch the films produced from the polymer blends of the present invention to
- 20 a greater extent provides for more economical use of film through the use of thinner stretch gauges. The films are able to be stretched to a greater level before the effects of strain hardening are observed when further stretching is not generally practical.

- The increased ability of the films made from the polymer blends of the present invention to
- 25 be stretched provides a concomitant increase in the films ability to maintain the stability of loads on wrapped pallets. The films produced from polymer blends of the present invention also advantageously demonstrate increased optical clarity which permits easier use of optical character recognition equipment, such as barcode readers, in the identification of the product wrapped under the stretch wrap film on the pallet.



Without wishing to be bound by theory it is believed that the addition of the particular low density polyethylenes described to the linear low density polyethylene improves the properties of the linear low density polyethylene film by the following mechanism. During the film blowing process, the polymer melt is extruded as a thin-walled cylinder that is subjected to extensional stress. The further thinning of the film and induction of a degree of orientation among the polymer chains permit the film to rapidly solidify and results in extremely rapid crystallisation whilst the partially oriented polymer melt is under extensional stress. As the molten film is cooled, crystallisation is believed to initially occur in regions of high molecular weight, lightly branched chains of linear low density polyethylene. Crystallisation fronts subsequently propagate through the molten film. It is believed that the crystallisation process may be usefully considered in two stages, primary and secondary. The primary crystallisation process is believed to form a network of oriented lamellae, which is followed by a secondary crystallisation within the highly supercooled film and which continues until an equilibrium level of crystallinity is achieved. It is believed that the minor component of low density polyethylene dispersed through the polymer blend acts to partially disrupt this primary crystallisation process, therefore altering the morphology created in the film. The changes in the crystalline morphology may be inferred from a decrease observed in crystallisation-induced haze which suggests a decrease in the average size of the crystallites. Changes in the intensity of x-ray scattering at low angles (SAXS) are consistent with this theory.

20

The efficacy of the low-density polyethylene modifier has been found to be greater with low density polyethylenes having higher molecular weight and higher degrees of long chain branching. It is believed that it is the small amount of extremely high molecular weight, highly long-chain branched molecules that provide the modification to the morphology of the polyethylene in a manner that is particularly advantageous to the stretch wrap properties as have been described above.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps

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but not the exclusion of any other integer or step or group of integers or steps.

The present invention is further described by reference to the following non-limiting examples.

5

### Example 1

An LLDPE base resin was produced in a gas-phase (Unipol) reactor with the comonomer being 1-hexene. The resin had a melt flow index (MFI) at 190°C and 2.16 kg mass of 1.0  
10 g/600s and a density at 25°C of 920 kg/m<sup>3</sup>. The LDPE used was produced in a high pressure autoclave reactor. The LDPE had the following properties:

	Melt Index	1.7 g/600s
	Density	918 kg/m <sup>3</sup>
15	M <sub>w</sub> /M <sub>n</sub>	23
	M <sub>z</sub>	3.5 x 10 <sup>6</sup> g/mol
	Long Chain Branch Frequency	3.5 /1000C
	HMW Fraction over M <sub>w</sub> 5 x 10 <sup>5</sup>	10.8% of LDPE

20 A blend of the LLDPE and LDPE at the level of 2% (w/w) of LDPE was prepared on a compounding extruder. Films were produced at 21-22 μm gauge on a blown film line typical of those used in industry, a 90 mm Battenfeld extruder fitted with a 400 mm oscillating die with a 2.4 mm die gap, and the film was blown at a blow up ratio of 2.8. The films contained, in addition, 4% (w/w) of a polyisobutene cling modifier (BP Hyvis 30, with a  
25 molecular weight of approximately 3000 g/mol) added during processing.

The films were tested using an instrumented stretch wrapper based on a LANTECH GP2000 in addition to all standard film tests. Standard film properties are shown in Table 1, while Table 2 lists the results of the automated stretch wrap tests.

30

**Example 2**

An LLDPE base resin of Example 1 was modified with an LDPE having the properties listed below:

5

Melt Index	1.6g /600s
Density	921 kg/m <sup>3</sup>
M <sub>w</sub> /M <sub>n</sub>	23
M <sub>z</sub>	2.4 x 10 <sup>6</sup> g/mol
10 Long Chain Branch Frequency	3.6 /1000C
HMW Fraction over M <sub>w</sub> 5 x 10 <sup>5</sup>	5.2% of LDPE

A blend of the above two polyolefins with a level of 4% (w/w) of LDPE was prepared on a compounding extruder. Films were produced and tested in accordance with Example 1.

15 Standard film properties are shown in Table 1, while Table 2 lists the results of the automated stretch wrap tests.

**Example 3**

20 The LLDPE base resin of Example 1 was blended with a LDPE having the properties listed below:

Melt Index	1.0g /600s
Density	922 kg/m <sup>3</sup>
25 M <sub>w</sub> /M <sub>n</sub>	7.4
M <sub>z</sub>	1.0 x 10 <sup>6</sup> g/mol
Long Chain Branch Frequency	2.4 /1000C
HMW Fraction over M <sub>w</sub> 5 x 10 <sup>5</sup>	1.8% of LDPE

30 A blend of the above two polyolefins containing a level of 5% (w/w) of LDPE was prepared

on a compounding extruder. Films were produced and tested in accordance with Example 1. Standard film properties are shown in Table 1, while Table 2 lists the results of the automated stretch wrap tests.

5

**Table 1**

Example	Haze (%)	Gloss (units)	NAS (units)	Puncture Energy (J)
100 % LLDPE	5.3	81	3.8	3.0
Example 1	3.0	87	1.9	2.9
10 Example 2	3.6	80	3.1	3.1
Example 3	6.1	77	4.6	3.1

**15 Example 4**

A LLDPE resin as of Examples 1-3 was modified with the same LDPE used in Example 1. A blend of the two polymers with a level of 1.5% (w/w) of LDPE was prepared by tumble blending.

20

Films from this blend were produced at an average gauge of 21  $\mu\text{m}$  on a Reifenhäuser blown film extrusion line. The film line extruder was of 70 mm diameter with a L/D ratio of 30, with a grooved barrel feed section and a barrier screw incorporating both dispersive and distributive mixing elements at the discharge end. The die diameter was 350 mm with a 2.6 mm die gap. Film was produced at a blow up ratio of 2.3. The films contained, in addition, 25 5 % (w/w) of a polyisobutylene cling additive (BP Hyvis 30) added by direct injection through the screw into the feed section of the extruder.

The films were aged for 7 days, then tested on a LANTECH GP2000 instrumented stretch 30 wrapper. The results are shown in Table 2 below.

**Example 5**

A blend of the same polymers as in Example 4 was tumble blended to give 4.5% (w/w) of the LDPE. Films were produced and tested in accordance with Example 4 and the results listed in Table 2.

**Example 6**

A LLDPE resin as of Example 4 was tumble blended with a LDPE having the properties listed below:

	Melt Index	8 g /600 s
	Density	918 kg/m <sup>3</sup>
	M <sub>w</sub> /M <sub>N</sub>	25
15	M <sub>z</sub>	4.0 x10 <sup>6</sup> g/mol
	Long Chain Branch Frequency	3.6 /1000C
	HMW Fraction over M <sub>w</sub> 5x10 <sup>5</sup>	7.8%

A blend of the two polymers was produced with a level of 4.5% (w/w) LDPE by tumble blending. Films were produced and tested in accordance with Example 4 and the results listed in Table 2.

**Example 7**

25 A LLDPE resin as of Example 4 was tumble blended with a LDPE having the properties listed below:

	Melt Index	0.3 g /600 s
	Density	921 kg/m <sup>3</sup>
30	M <sub>w</sub> /M <sub>N</sub>	9.0

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$M_z$	$2.0 \times 10^6$ g/mol
Long Chain Branch Frequency	3.2 /1000C
HMW Fraction over $M_w$ $5 \times 10^5$	3.0%

5 A blend of the two polymers was produced with a level of 4.5% (w/w) LDPE by tumble blending. Films were produced and tested in accordance with Example 4 and the results listed in Table 2.

### Example 8

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A LLDPE resin as of Example 4 was tumble blended with a LDPE having the properties listed below:

	Melt Index	1.0 g /600 s
15	Density	921 kg/m <sup>3</sup>
	$M_w/M_N$	7.4
	$M_z$	$1.0 \times 10^6$ g/mol
	Long Chain Branch Frequency	2.7 /1000C
	HMW Fraction over $M_w$ $5 \times 10^5$	1.8%

20

A blend of the two polymers was produced with a level of 4.5% (w/w) LDPE by tumble blending. Films were produced and tested in accordance with Example 4 and the results listed in Table 2.

25

Table 2

Example	Effective Stretch (%)	Maximum Stretch (%)	Adhesion @ 400% stretch <sup>1)</sup>
100 % LLDPE	335	510	3
Example 1	380	560	9
Example 2	355	510	5
30 Example 3	330	495	0

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Example 4	420	600	9
Example 5	400	570	9
Example 6	330	535	7
Example 7	320	575	4
5 Example 8	350	515	4

<sup>1)</sup> Adhesion was assessed on a scale of 0 -9 where:

0 = Non-existent

3 = Poor

10 6 = Good

9 = Excellent

### Example 9

15 The average unwinding force of a stretch wrap film roll is a measure of the cling, and therefore when measured as a function of aging, it is a measure of the migration of cling modifier to the film surface. Table 3 compares the unwinding force for two rolls of film, measured throughout the period in which cling developed. The first film was prepared from an unmodified LLDPE and the second film prepared from a blend of the same LLDPE and

20 2 %(w/w) of the LDPE described in Example 1. Full development of cling was apparent for the modified composition substantially prior to that of the unmodified LLDPE.

**Table 3**

	Film Aging				
	1 day	3 days	5 days	7 days	10 days
25 100% LLDPE					
Unwinding Force (N)	4.9	13.7	19.6	22.6	26.5
Example 1					
Unwinding Force (N)	3.9	17.7	23.5	25.5	24.5

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## CLAIMS

1. A polymer blend comprising a linear low density polyethylene, further including from 0.5 to 5% (w/w) of a low density polyethylene wherein said low density polyethylene has a long-chain branch frequency of greater than 2 /1000C and a molecular weight fraction ( $M_w$ ) over  $5 \times 10^5$  g/mol of greater than 2.5% by weight of the low density polyethylene, and further including an effective amount of a cling additive.
2. A polymer blend according to claim 1 wherein the linear low density polyethylene has been polymerized in gas-phase reactors using a heterogeneous catalyst.
3. A polymer blend according to either claim 1 or 2 wherein the linear low density polyethylene has been polymerized in a gas-phase reactor using a Ziegler/Natta catalyst system and has a density in the range of from 913 to 930 kg/m<sup>3</sup> and a melt index in the range of from 0.4 to 2.5 g/600s.
4. A polymer blend according to any of claims 1 to 3 wherein the linear low density polyethylene is a copolymer of ethylene and an alpha-olefin selected from the group consisting of propene, butene, 4-methyl-pentene, hexene, octene and decene.
5. A polymer blend according to any of claims 1 to 4 wherein the low density polyethylene has been produced by free radical polymerisation via a high pressure autoclave process.
6. A polymer blend according to any of claims 1 to 5 wherein the low density polyethylene has been polymerised under conditions which favour the production of polymers with broad molecular weight distributions and a high degree of long-chain branching.
7. A polymer blend according to any of claims 1 to 6 wherein the low density polyethylene has a bi-modal molecular weight distribution and a high degree of long-chain



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branching in the high molecular weight fraction of the low-density polyethylene.

8. A polymer blend according to any of claims 1 to 7 wherein the low density polyethylene selected for use in the compositions of the present invention has a melt index in the range of from 0.1 to 7 g/600s.

9. A polymer blend according to any of claims 1 to 8 wherein the low density polyethylene selected for use in the compositions of the present invention has a melt index in the range of from 0.3 to 4 g/600s.

10

10. A polymer blend according to any of claims 1 to 9 wherein the low density polyethylene has a density in the range of from 913 to 930 kg/m<sup>3</sup>.

11. A polymer blend according to any of claims 1 to 10 wherein the low density polyethylene has a density in the range of from 917 to 922 kg/m<sup>3</sup>.

12. A polymer blend according to any of claims 1 to 11 wherein the low density polyethylene has a polydispersity index ( $M_w/M_n$ ) of greater than 15.

13. A polymer blend according to any of claims 1 to 12 wherein the low density polyethylene has a polydispersity index ( $M_w/M_n$ ) of greater than 22.

14. A polymer blend according to any of claims 1 to 13 wherein the  $M_z$  value of low density polyethylene is preferably greater than  $2 \times 10^6$  g/mol.

25

15. A polymer blend according to any of claims 1 to 14 wherein the  $M_z$  value of low density polyethylene is preferably greater than  $3 \times 10^6$  g/mol.

16. A polymer blend according to any of claims 1 to 15 wherein the low density polyethylene has a long-chain branch frequency as determined by <sup>13</sup>C nuclear magnetic

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resonance spectroscopy of greater than 3 /1000C.

17. A polymer blend according to any of claims 1 to 16 wherein the low density polyethylene has a molecular weight fraction ( $M_w$ ) over  $5 \times 10^5$  g/mol of greater than 5% by weight of the low density polyethylene.

18. A polymer blend according to any of claims 1 to 17 wherein the low density polyethylene has a high molecular weight fraction ( $M_w$ ) over  $5 \times 10^5$  g/mol of greater than 10% by weight of low density polyethylene.

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19. A polymer blend according to any of claims 1 to 18 wherein the cling additive is selected from the group consisting of low molecular weight polyisobutylenes or polybutenes, atactic polypropylenes, glycerol monooleate and sorbitan monooleate.

15 20. A polymer blend according to any of claims 1 to 19 wherein the cling additive is a low molecular weight polyisobutylene.

21. A polymer blend according to any of claims 1 to 20 wherein the cling additive is a low molecular weight poly(isobutylene-co-butylene)

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22. A polymer blend according to any of claims 1 to 21 wherein the low molecular weight polyisobutylene has a number average molecular weight in the range of from 500 to 3,000 g/mol.

25 23. A polymer blend according to any of claims 1 to 22 wherein the cling additive is present in the modified linear low density polyethylene in an effective amount, in the range of from 0.1% to 7% (w/w).

24. A monolayer film manufactured from a polymer blend comprising a linear low density  
30 polyethylene, further including from 0.5 to 5% (w/w) of a low density polyethylene wherein

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said low density polyethylene has a long-chain branch frequency of greater than 2 /1000C and a molecular weight fraction ( $M_w$ ) over  $5 \times 10^5$  g/mol of greater than 2.5% by weight of the low density polyethylene, and further including an effective amount of a cling additive.

5 25. A monolayer film according to claim 24 wherein the linear low density polyethylene has been polymerized in gas-phase reactors using a heterogeneous catalyst.

26. A monolayer film according to either claim 24 or 25 wherein the linear low density polyethylene has been polymerized in a gas-phase reactor using a Ziegler/Natta catalyst system  
10 and has a density in the range of from 913 to 930 kg/m<sup>3</sup> and a melt index in the range of from 0.4 to 2.5 g/600s.

27. A monolayer film according to any of claims 24 to 26 wherein the linear low density polyethylene is a copolymer of ethylene and an alpha-olefin selected from the group consisting  
15 of propene, butene, 4-methyl-pentene, hexene, octene and decene.

28. A monolayer film according to any of claims 24 to 27 wherein the low density polyethylene has been produced by free radical polymerisation via a high pressure autoclave process.

20

29. A monolayer film according to any of claims 24 to 28 wherein the low density polyethylene has been polymerised under conditions which favour the production of polymers with broad molecular weight distributions and a high degree of long-chain branching.

25 30. A monolayer film according to any of claims 24 to 29 wherein the low density polyethylene has a bi-modal molecular weight distribution and a high degree of long-chain branching in the high molecular weight fraction of the low-density polyethylene.

31. A monolayer film according to any of claims 24 to 30 wherein the low density  
30 polyethylene selected for use in the compositions of the present invention has a melt index in

the range of from 0.1 to 7 g/600s.

32. A monolayer film according to any of claims 24 to 31 wherein the low density polyethylene selected for use in the compositions of the present invention has a melt index in  
5 the range of from 0.3 to 4 g/600s.

33. A monolayer film according to any of claims 24 to 32 wherein the low density polyethylene has a density in the range of from 913 to 930 kg/m<sup>3</sup>.

10 34. A monolayer film according to any of claims 24 to 33 wherein the low density polyethylene has a density in the range of from 917 to 922 kg/m<sup>3</sup>.

35. A monolayer film according to any of claims 24 to 34 wherein the low density polyethylene has a polydispersity index ( $M_w/M_n$ ) of greater than 15.

15

36. A monolayer film according to any of claims 24 to 35 wherein the low density polyethylene has a polydispersity index ( $M_w/M_n$ ) of greater than 22.

37. A monolayer film according to any of claims 24 to 36 wherein the  $M_z$  value of low  
20 density polyethylene is preferably greater than  $2 \times 10^6$  g/mol.

38. A monolayer film according to any of claims 24 to 37 wherein the  $M_z$  value of low density polyethylene is preferably greater than  $3 \times 10^6$  g/mol.

25 39. A monolayer film according to any of claims 24 to 38 wherein the low density polyethylene has a long-chain branch frequency as determined by <sup>13</sup>C nuclear magnetic resonance spectroscopy of greater than 3 /1000C.

40. A monolayer film according to any of claims 24 to 39 wherein the low density  
30 polyethylene has a molecular weight fraction ( $M_w$ ) over  $5 \times 10^5$  g/mol of greater than 5% by

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weight of the low density polyethylene.

41. A monolayer film according to any of claims 24 to 40 wherein the low density polyethylene has a high molecular weight fraction( $M_w$ ) over  $5 \times 10^5$  g/mol of greater than 5 10% by weight of the low density polyethylene.

42. A monolayer film according to any of claims 24 to 41 wherein the cling additive is selected from the group consisting of low molecular weight polyisobutylenes or polybutenes, atactic polypropylenes, and glycerol monooleate.

10

43. A monolayer film according to any of claims 24 to 42 wherein the cling additive is a low molecular weight polyisobutylene.

44. A monolayer film according to any of claims 24 to 43 wherein the cling additive is a 15 low molecular weight poly(isobutylene-co-butylene)

45. A monolayer film according to any of claims 24 to 44 wherein the low molecular weight polyisobutylene has a number average molecular weight in the range of from 500 to 3,000 g/mol.

20

46. A monolayer film according to any of claims 24 to 45 wherein the cling additive is present in the modified linear low density polyethylene in an effective amount, in the range of from 0.1% to 7% (w/w).

25 47. A monolayer film according to any one of claims 24 to 46 wherein the monolayer film has been manufactured in a blown film process.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00302

**A. CLASSIFICATION OF SUBJECT MATTER**Int Cl<sup>6</sup>: C08L 23/04, 23/06, 23/08; C08J 5/18; B65D 71/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**Minimum documentation searched (classification system followed by classification symbols)  
C08L 23/04, 23/06, 23/08; C08J 5/18; B65D 75/-, 71/06, 19/44; B65B 11/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Derwent (keywords: LLDPE, LDPE, cling wrap, stretch wrap)**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94/26816 A (EXXON CHEMICAL PATENTS INC.) 24 November 1994 (see entire document, in particular page 1 lines 28-29, page 2 lines 16-35, page 12 line 34—page 13 line 10, page 17 lines 12-21, page 18 lines 28-33, page 19 lines 25-29)	1-47
Y	(see page 13 lines 3-17 etc) Derwent Abstract Accession No. 84-143579/23, Class P73, JP 59075933 A (TOKUYAMA SODA KK) 28 April 1984	1-47
X,Y	(see entire abstract) Mark Alger, Polymer Science Dictionary, Second Edition, 1997, Chapman & Hall, London	1-47
Y	(see page 296 "low density polyethylene")	

☒ Further documents are listed in the continuation of Box C☒ See patent family annex

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
28 May 1999Date of mailing of the international search report  
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## INTERNATIONAL SEARCH REPORT

International application No. .

PCT/AU 99/00302

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 53995 A (THE GOODYEAR TIRE & RUBBER COMPANY) (see entire document, in particular page 2 lines 32-34, claims 1-4)	1-47
X	Derwent Abstract Accession No. 95-048960/07, Class V04, JP 06329849 A (NIPPON UNICAR CO LTD) 29 November 1994 (see entire abstract)	1-47
X Y	US 4587303 A (Turtle B. L.) 6 May 1986 (see the entire document, in particular column 2 line 32 to column 4 line 6, claim 7) (see column 3 line 67 to column 4 line 2)	1-47
Y	EP 6110 A (UNION CARBIDE CORPORATION) 9 January 1980 (see in particular claim 5, page 2 line 8- page 3 line 38, page 32 lines 32-34, page 36 line 23 to page 37 line 18, examples 19-28, etc)	1-47
A	EP 80198 A (THE DOW CHEMICAL COMPANY) 1 June 1983 (see entire document, in particular the abstract, page 4 lines 9-24, page 5 line 22-page 6 line 5, page 9 line 10-page 12 line 19, claim 8 etc.)	1-47
A	US 4504434 A (Cooper B. A.) 12 March 1985 (see entire patent, in particular column 2 lines 46-68, column 5 lines 40-46, column 6 lines 19-22 and 41-50, example 1 etc.)	1-47
A	Derwent Abstract Accession No. 92-343566/42, Class P73, JP 04246536 A (GUNZE KK) 2 September 1992 (see entire abstract)	1
A	EP 287272 A (MOBIL OIL CORPORATION) 19 October 1988 (see entire document, in particular page 3 lines 6-14, page 2 lines 40-44)	1-47
A	Derwent Abstract Accession No. 93-056432/07, Class A17, KR 9204619 B (CLEAN WRAP CO LTD) 12 June 1992 (see entire abstract)	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.  
PCT/AU 99/00302

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
WO	9426816	AU	69112/94	CA	2162681	CN	1126481
		CN	1126483	EP	698044	EP	699219
		EP	877051	WO	9426793		
EP	53995	BR	8107908	CA	1188447	JP	57117548
		MX	159223	US	4362835	ZA	8107781
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EP	80198	AU	90156/82	CA	1189218	GB	2110700
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US	4504434	US	4425268	US	4436788		
EP	287272	CA	1323973	US	5273809	US	5617707
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		AU	45657/79	BR	7901938	CA	1131838
		DK	1314/79	ES	479100	FI	791043
		GR	72417	IN	151072	JP	54154466
		NO	791067	NZ	190060	PT	69416
		ZA	7901365	US	4243619		
JP	06329849	NONE					
KR	9204619	NONE					
JP	04246536	NONE					
JP	59075933	NONE					

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